Behaviour of major and trace elements and fractionation of REE under tropical weathering of a typical apatite-rich carbonatite from Brazil

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Abstract

Detailed petrographical, mineralogical and geochemical studies have been carried out on a weathering profile developed on the phosphate-rich carbonatite of Juquind (Brazil). Four weathering trends could be distinguished by means of the relationships between primary (apatites, dolomite, phlogopite, magnetite and barite) and secondary (apatites, gorceixite, wavelite, calcite and Fe–Mn-oxyhydroxides) minerals. Local isovolumetric and isoelemental weathering processes allowed us to estimate chemical mass balances within some weathering trends. Except for Al in one profile, all the major and trace elements are mobile and transferred as a result of weathering of the primary minerals. The REE patterns of each primary/secondary mineral show that the weathering processes fractionate LREE and HREE. Relationships between REE content and the water/rock ratio may explain the various REE contents and distribution curves exhibited by the secondary minerals. Precipitation of secondary minerals in open microsystems (i.e., veins and fissures) appears to be associated with REE depletion and fractionation. In contrast, crystallization of secondary minerals within the intragranular micropores may result in a significant preservation of the REE content and distribution of the primary minerals being replaced. Moreover, poorly crystallized and flaky secondary minerals act as traps for REE.

1. Introduction

Intrusions of alkaline rocks are often associated with carbonatites enriched in phosphate minerals [1]. P₂O₅ contents of phosphate-rich carbonatites typically range from 5 to 18%. In order to evaluate the possibility that carbonatites are a significant source of P for sedimentary phosphates and to understand the migration processes of phosphorus during weathering, a large suite of phosphate minerals present in the Mesozoic alkaline complexes located in the southeastern part of the Paraná Basin (Brazil) has been subjected to an exhaustive geochemical study. Phosphate minerals were also studied in the overlying weathering mantle, which ranges in thickness from 10 to 80 m.

Many studies dealing with the weathering of apatite-rich carbonatites located in Russia, Africa and...
Brazil [2–4] have been published. These essentially describe the transformation of primary apatite into various calc-aluminous phosphates. REE behaviour during weathering processes has been extensively studied in a variety of weathering profiles [5–11]. Chemical mass balance calculations from the literature have been carried out on bulk rock samples in particular. These calculations show that LREE are generally less mobile than HREE. This induces a relative enrichment in LREE relative to the HREE (high La/Yb ratio) in highly weathered material.

The object of the present work is to examine the weathering patterns of a typical apatite-rich carbonatite and to characterize the behaviour of the major and trace element and the REE during weathering. We chose to study the representative Juquiá complex, the petrography, mineralogy and geochemistry of which is well known [12–15].

2. Geographical and geological setting

The Juquiá complex, which lies 270 km southwest of São Paulo, was emplaced 127 m.y. ago [16] in the Precambrian gneisses of the South American craton. The rocks of the complex are spatially distributed following a nearly concentric pattern, with alkaline (nepheline syenites, syenodiorites, ijolites, clinopyroxenites) and mafic-ultramafic rocks surrounding a core of apatite rich carbonatite.

3. Methods

The fresh rock and the weathering profile were carefully sampled. Pure or nearly pure separates of the minerals present in the parent rock and weathering profile were obtained using heavy liquids, selective dissolution and microsampling (microdrill). A detailed petrographical and mineralogical study of the samples was carried out. Optical microscopy, a scanning electron microprobe (JEOL 35CF with Tracor analysis capability), X-ray diffractometry (Philips 1729, CoKα or CuKα radiation), electron microprobe chemical analysis (Camebax) and inductively coupled plasma atomic emission spectrometry analysis (ICP–AES) were used for characterization of the bulk samples and mineral separates. The apatites were further characterized with infrared spectrometry (Fourier-transformed Nicolet 20 SXB with a precision frequency of $10^{-1}$–$10^{-2}$).

REE analyses of pure or nearly pure mineral separates (previously analyzed by X-ray diffraction, infrared spectrometry, etc.) were performed using a Thomson THN 206 single-collector mass spectrometer. Chemical separations were obtained by cation exchange with Dowex resin (50X8, 200–400 mesh) and by reverse chromatography (HDEHP fixed on Teflon powder) of samples previously spiked and dissolved in a HCl–HNO₃–HF mixture. Several samples of the same mineralogical type were been sampled, and each sample was analyzed for REE twice (replicates) in order to test the validity of the analysis. The analytical uncertainty, as indicated by the replicate analyses, is about 1%.

4. General organization of the profile: Field observations

The weathering profile developed from the apatite-rich carbonatite is 40 m thick and exhibits three main horizons:

1. The lowermost horizon corresponds to the fresh, unweathered, parent carbonatite.
2. The overlying horizon is a light brown to ochreous saprolite (weathered rock in which the parent rock structures are preserved). The boundary between the fresh rock and the saprolite is sharp and well defined, although it is irregular (wavy).
3. The uppermost horizon is a brown to red clay-rich layer in which the original structure of the parent rock is no longer recognizable.

In-situ origin of the uppermost horizon is questionable, and our study was therefore limited to the lowermost and intermediate horizons, which can readily be shown to have formed as a result of in-situ chemical weathering of the Juquiá carbonatite.

5. Petrography and mineralogy of the parent rock

The Juquiá carbonatite has been the subject of several works [12–16], and thus we have chosen to present a summary of the results and discussion regarding its origin and emplacement.
atite is composed of abundant dolomite (≈ 35 vol%) and apatite (> 50 vol%), usually well-segregated in the rock and associated with rare micas, magnetite and barite. The dolomite is uniformly iron-rich (Table 1A) and occurs as clusters of euhedral crystals (100–200 μm in size). Two generations of magmatic apatite can be distinguished. The first type (referred to as type 1 apatite) is a hydroxyfluorap-

Table 1

(A) Chemical compositions (%) of minerals of the Juquia carbonatite and of the weathering profile as determined by electron microprobe (except for (•) CO₂ (%), H₂O+ (%), and Cl (%) which were derived from arc spectrometry and infrared spectrometry analyses and for (••) CO₂ (%) which was calculated following Scheib et al. [17])

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Dolomite</th>
<th>Apatite</th>
<th>Magnetite</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Carbonate matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>0.62</td>
<td>0.00</td>
<td>0.20</td>
<td>42.82</td>
<td>21.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.11</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.42</td>
<td>0.07</td>
<td>0.06</td>
<td>0.51</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>BaO</td>
<td>0.08</td>
<td>0.10</td>
<td>0.08</td>
<td>0.10</td>
<td>0.20</td>
<td>0.63</td>
</tr>
<tr>
<td>MgO</td>
<td>22.35</td>
<td>26.04</td>
<td>0.05</td>
<td>0.07</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.47</td>
<td>0.07</td>
<td>0.06</td>
<td>0.06</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.00</td>
<td>0.97</td>
<td>0.21</td>
<td>0.01</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.31</td>
<td>5.68</td>
<td>0.05</td>
<td>0.34</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>F</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>S (tot.)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>2.66</td>
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<td>CO₂</td>
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<td>0.00</td>
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<tr>
<td>H₂O</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

N, N* and N# = number of analyses

(B) REE contents of samples of the carbonatite parent rock, primary dolomite, type 1 apatite, type 1 and 2 apatite, phlogopite micas and barite, and secondary minerals (mass spectrometry, in ppm).
Fig. 1. Photomicrographs of thin sections. (A) Magmatic hydroxyfluorapatite ($a_1$) surrounded by rings of post-magmatic Na-rich carbonate-fluorapatite ($a_2$). Scale bar = 50 μm; crossed polars. (B) Dissolution of magmatic dolomite ($d$) inducing formation of septae of type 1 Fe–Mn products ($s$); $v$ = voids; arrows = hacksaw dissolution features. Scale bar = 10 μm; plane light. (C) Pseudomorphic replacement of type 3 apatite ($a_3$) by type 4 apatite ($a_4$); $a_2$ = type 2 apatite. Scale bar = 10 μm; plane light. (D) Fissure filled by type 5 ($a_5$) and type 6 ($a_6$) apatites; $ba$ = barite. Scale bar = 0.5 cm; plane light. (E) Mica-like gorgeixite ($g$) associated with gorgeixite matrix ($mg$); $v$ = voids. Scale bar = 500 μm; plane light. (F) Diamond-shape voids ($v$) created by magnetite dissolution are filled with type 2 Fe–Mn products ($t_2$). Scale bar = 5 μm; plane light.
apatite with a low carbonate content (Table 1A) which occurs as euhedral crystals (50–100 μm) organized in a fluidal texture between the clusters of dolomite. The second type, referred to as type 2 apatite, is a Na-rich carbonate–fluorapatite occurring as rims around crystals of type 1 apatite (Fig. 1A, Table 1A). Both types result from sequential crystallization of apatite during the emplacement of the carbonatite [13,14]. The mica phase is a phlogopite with a high Fe content (Table 1A) and is concentrated in centimetre- to metre-sized lenses which are non-uniformly distributed throughout the carbonatite. Magnetite always occurs as small isolated euhedral crystals (50 μm) and displays a high Ti content (Table 1A). The carbonatite mineral assemblage described above is crosscut by veins of barite (Table 1A) (a typical feature of such intrusive complexes) related to hydrothermal events [18].

Previous studies [13,14] have shown that (1) type 1 apatite is characterized by a typical relative enrichment in LREE (also observed in the dolomite) while the crystallization of type 2 apatite is associated with another magmatic fluid enriched in M–HREE with respect to type 1 apatite, (2) phlogopite micas have been affected by this same fluid, and that (3) the hydrothermal barite contains less REE than the other carbonatite minerals and shows a marked relative enrichment in HREE (Table 1B, Fig. 2A). These REE patterns are explained as the result of a progressive supersaturation of the initial carbonatite magma with respect to carbonate and phosphate [14]. As a consequence, the Juquii parent rock REE pattern shows a marked enrichment in M–HREE, which distinguishes it from most other carbonatites that are only enriched in LREE relative to the HREE [18,19].

6. Weathering trends and local element mobility in the saprolite

Because of the lack of evidence for any particular element being preserved (isoelement) throughout the weathering process, conventional mass balance calculations cannot be used to quantify chemical transfer during weathering. Even the isotitanium procedure is unsuitable, because of the transfer of TiO₂ as a result of magnetite weathering (see Section 6.4). However, detailed petrographical and mineralogical observations indicate that four different weathering trends can be distinguished within the saprolite. Each trend is composed of a suite of several secondary minerals which exhibit specific textural habits and
relationships with the primary minerals and allow us, to some extent, to undertake mass-balance calculations on a local and small scale. For these calculations we used the isovolume mass balance equation (% change = [(C_{w,w} · \rho_w)/(C_{w,pr} · \rho_{pr}) - 1] · 100) and the isoelement equation (% change = [(C_{w,w}/C_{w,pr})/(C_{w,pr}/C_{w,pr}) - 1] · 100). In these equations, C_{w,w} and C_{w,pr} are the element (e) concentrations in the secondary mineral (w) and in the parent mineral (pr) respectively, C_{w,w} and C_{w,pr} are the concentrations of the isoelement in the secondary mineral (w) and in the parent mineral (pr) respectively, and \rho_w and \rho_{pr} are the respective mineral densities.

6.1. Dolomite weathering trend

The dolomite weathering trend corresponds to the succession of secondary minerals formed as a consequence of dolomite dissolution. The top part of the parent carbonatite is characterized by the development of small (< 1 cm wide) cracks and fissures filled with sparry crystals of low-Mg calcite (Table 1A). Because these low-Mg calcite-filled cracks are not observed elsewhere in the parent rock or in the saprolite, they must have formed early in the weathering process. However, precise time relationships with respect to the weathering phases present in the overlying saprolite are unclear. As dolomite crystals dissolve, in the lower part of the saprolite, they are gradually replaced by septae [20] of goethite and amorphous Fe-Mn-rich products, referred to as type 1 Fe-Mn products (Table 1A and Fig. 1B). These septae (with walls of up to 1 mm in thickness) constitute a framework which, together with the unaffected type 1 and 2 apatites, forms a very rigid structure. In the uppermost part of the profile, the saprolite presents a mixture of goethite and hematite, characterized by Si and Mn contents (Table 1A) that are higher than those of the type 1 Fe-Mn products.

REE patterns of the low-Mg calcite indicate a typical depletion of all REE compared to the dolomite, while type 1 and type 3 Fe-Mn products are enriched in REE (Fig. 2B). In addition, type 3 Fe-Mn products contain higher amounts of REE than type 1 Fe-Mn products (especially MREE and HREE, and larger La/Yb ratios, Table 1B), and show homogeneous REE enrichments compared to the dolomite while type 1 Fe-Mn products exhibit a depletion of HREE compared to LREE. Calcite and type 1 and type 3 Fe-Mn products show a slight positive Ce and Er anomaly compared to dolomite.

The accumulation of low-Mg calcite in fissures affecting the top part of the fresh carbonatite indicates that some CO_3^{2-}, Ca^{2+} and Mg^{2+} ions released by the dissolution of dolomite are moving downward into the top part of the fresh rock where dolomite is still unweathered. However, the Ca/Mg ratio of the dolomite (Ca/Mg = 1.3) is different from that of the low-Mg calcite (Ca/Mg = 28), indicating that only a small part of the magnesium released by the dolomite is used by the low-Mg calcite. Although petrographic observations show that type 1 Fe-Mn products from the bottom of the profile are closely related to dolomite dissolution, chemical analyses of type 1 and type 3 Fe-Mn products suggest that they contain elements coming from the upper part of the profile. The respective volumes of the dissolved dolomite and associated type 1 Fe-Mn products can be estimated from petrographic observations by means of measurement of the respective surfaces of the dissolved dolomite (i.e., dissolution pore surface) and the type 1 Fe-Mn products present in these dissolution pores (type 1 Fe-Mn products surface/dissolved dolomite surface = 0.38). Note that we ignore the intrinsic porosity of the type 1 Fe-Mn products. The combined use of these volumes and the chemical compositions derived from microprobe analysis (Table 1A) yields an approximate reaction equation for the formation of the septae (type 1 Fe-Mn products) that is valid on a microscale:

\[
\begin{align*}
(Ca_{0.473}Mg_{0.505}Fe_{0.015}Mn_{0.006})CO_3 \\
+ 0.801Fe_{(tot,aqu)} + 0.138Mn_{(tot,aqu)} + 0.5H_2O \\
\rightarrow (Fe_{0.816}Mn_{0.194})OOH + 0.473Ca_{(tot,aqu)} \\
+ 0.505Mg_{(tot,aqu)} + CO_2
\end{align*}
\]

The oxyhydroxide formula ((Fe_{0.816}Mn_{0.194})OOH) does not ensure a volume that is equal to that of the dolomite formula because Fe-Mn products fill 38% of the initial volume of the dissolved dolomite. Therefore, taking the respective molar volumes of dolomite, goethite and manganite into account, some
Fe and Mn would have to be imported for the formation of septae. In order to approximate the behaviour of elements during the dolomite dissolution, mass balance calculations were carried out using isovolume, which is supported by petrographical observations. The respective mineral densities have been calculated from X-ray diffraction and chemical analyses using molar volumes and molar weights found in Robe et al. [21]. The results (Table 2) show that no element can be considered as an isoelement. Calcium, strontium and magnesium are leached, while manganese, iron, aluminium, titanium, sodium and barium are accumulated. Both approaches remain rough estimates and are associated with significant uncertainties. However, the results indicate that Fe–Mn products formed as pseudomorphic replacement of dolomite, by means of microtransfers of elements and associated with Fe and Mn macrotransfers; this may occur even as dissolution of dolomite is still in progress. The chemical composition of type 3 Fe–Mn products suggests that the Fe–Mn products act as traps for several trace elements, among which is silicon. Results of mass balance calculations confirm a gain of all REE, with a greater gain of LREE (except La) compared to the MREE and HREE, during the transformation of dolomite into type 1 Fe–Mn products.

### Table 2
Comparative mobility of the major and trace elements in mineralogical trends I, III and IV (calculations made using isovolume for dolomite/type 1 Fe–Mn product and magnetite/type 2 Fe–Mn product transformations, and Al as an isoelement for the two other transformations)

<table>
<thead>
<tr>
<th>Parent mineral</th>
<th>Secondary mineral</th>
<th>Relative losses (%)</th>
<th>Relative gains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>Type 1 Fe-Mn-products</td>
<td>Mg, Ca, Sr</td>
<td>P</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Type 2 Fe-Mn-products</td>
<td>Mg, Ca, Sr</td>
<td>Mg</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>Micas-like Gorceixite</td>
<td>Mg, K, Si, Mn, Fe</td>
<td>all REE</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>Gorceixite Matrix</td>
<td>Mg, K, Si, Eu→Dy</td>
<td>Fe, La→Sm, Er→Lu</td>
</tr>
</tbody>
</table>

6.2. Apatite weathering trend

This trend represents the dissolution of type 1 and type 2 primary apatites which induces the crystallization of different types of secondary apatites whose secondary origin was assessed by measurement of oxygen and carbon isotopic ratios [15]. The first secondary apatite, referred to as type 3 apatite, is a carbonate–fluorapatite (Table 1A) which occurs as needles perpendicular to the Fe–Mn septae and to the primary apatites and which is locally organized in ribbons (Fig. 1C). As weathering progresses in the uppermost part of the saprolite type 1 and type 2 apatites are weathered extensively. Type 3 apatite are locally covered by a translucent thin layer of apatite referred to as the type 4 apatite (Fig. 1C). Because of the thinness of this layer, only electron microprobe analyses could be performed on that generation of secondary apatite (Table 1A). The chemical composition of type 4 apatite is fairly close to that of type 3 apatite, except for slightly lower Sr contents. The last two generations of secondary apatites (referred to as type 5 and type 6 apatites) fill fissures and cracks that cut across the primary and secondary minerals previously described (Fig. 1D). Type 5 apatite is a fluorapatite (Table 1A) and consists of a dull, white, thin layer (0.01–1 cm) made up of very
thin fibres that are parallel to each other. Type 5 apatite is overlain by type 6 fluorapatite (Table 1A), which consists of two successive deposits of large (200–500 μm), globular, translucent crystals. The reaction rings observed between type 3 and type 4 apatites and between type 5 and type 6 apatites show that the type 4 and type 6 apatites represent a new stage of the weathering process.

Type 3 apatite shows an homogeneous REE distribution curve, with a small depletion of all REE (although more pronounced for the M–HREE, Fig. 2B), and a slight positive Ce anomaly and a negative Er anomaly with respect to the type 1 and 2 apatites (Table 1B). In contrast, the other secondary apatites (type 5 and 6) are characterized by a strong depletion of all REE and a negative Ce anomaly with respect to the type 1 and 2 apatites, and by a marked relative enrichment in LREE with respect to HREE (Fig. 2B), as also shown by the respective La/Yb ratios (Table 1B). A negative Ce anomaly with respect to the type 1 and 2 apatites is observed in type 5 apatite. The youngest secondary apatite (type 6 apatite) is enriched in REE compared to the type 5 apatite, confirming that it corresponds to a new stage of the weathering process.

Each generation of supergene apatites is characterized by a distinct textural habit that is related to the different conditions of crystallization. Large growth shapes generally occur in low-concentration environments. In contrast, microcrystalline shapes are favoured in highly supersaturated environments in which many crystallization nuclei may appear rapidly [22]. The chemical compositions of the type 3, 4, 5 and 6 apatites are close to those of type 1 apatite, with just slight variations in the major and trace elements. An exception occurs for the type 3 apatite, whose CO₂ content is higher, closer to the CO₂ content of type 2 apatite, while the type 5 and 6 apatites exhibit lower CO₂ contents that are typical of fluorapatites. Needles of type 3 apatite crystallized during the earlier stage of the weathering in a semi-closed system with a CO₂ fugacity high enough to be expressed within the lattice of the newly formed type 3 apatite. Thus, the high CO₂ content of type 3 apatite may simply be chemical memory from the primary apatite (type 2). The pure type 5 and type 6 apatites are only observed in fissures, where chemical macrotransfers prevail, and exhibit no chemical characteristics reminiscent of those of primary type 1 and type 2 apatites. The pore system enhances microtransfers of elements between primary and secondary minerals and seems to induce a type of chemical memory for some elements.

6.3. Phlogopite weathering trend

About 5% of the exposed saprolite occurs as local lenses of a very porous material composed of a mixture of goethite and gorceixite (Al–Ca–Ba-phosphate) together with relicts of primary apatites and barite. Gorceixite occurs as a continuous finely crystallized matrix or as a sheet-like mineral (Fig. 1E). The gorceixite–goethite matrix exhibits a porous microaggregated texture (20–100 μm thick) that is typical of oxic soils [20]. Its chemical composition (Table 1A) displays significant variations in Ti and Fe contents that may simply reflect a patchy distribution of micromottles of goethite or the presence of microrelicts of magnetite within the matrix. Sheets of mica-like gorceixite show systematic intragrain variations in chemical composition, from the periphery (gorceixite-type composition) to the centre (composition intermediate to phlogopite and pure gorceixite compositions) (Table 1A). This suggests that mica-like gorceixite probably formed as a pseudomorphic replacement of micas. Cracks and fissures are coated with needles (< 1 mm) of pure wavellite (Al-phosphate). Electron microprobe analyses of the peripheries of the primary apatite crystals show that their SiO₂ content is variable and higher (1.12% SiO₂) than that of type 1 or type 2 apatite (≈ 0.12%). In contrast, their Ca/P ratio remains unchanged, suggesting the presence of amorphous siliceous domains within the apatite grains.

Gorceixite matrix samples and one sample of mica-like gorceixite generally present a relative enrichment of all REE with respect to the phlogopite (Fig. 2C). The other two gorceixite pseudomorphs after micas are REE-enriched and characterized by a pronounced relative enrichment of LREE with respect to HREE (Fig. 2C). This is also shown by their La/Yb ratios and a positive cerium anomaly (Table 1B).

The formation of gorceixite and wavellite constitutes the phlogopite weathering trend. The first habit reflects progressive pseudomorphism after micas and
exhibits a high goethite content between the sheets. The second habit is organized into microaggregates, whose characteristics are close to those of stoichiometric gorceixite (perhaps reflecting greater crystallization or reorganization than the pseudomorphic replacement). These observations suggest that aluminium may be considered as an isoelement for local chemical mass balance calculations, as was done in other studies. Thus, mass balance calculations were conducted for the gorceixite matrix and the periphery of the mica-like gorceixite. In both cases, the results show gains of titanium, barium, strontium, calcium, manganese and sodium. Mica-like gorceixite formation is associated with a gain of LREE. Gorceixite matrix formation is associated with losses of all REE, but especially of the MREE and HREE. These apparent gains may be related to the presence of type 1 and 2 apatites, barite and magnetite close to the phlogopite micas. The gorceixite parent rock may thus be different from the carbonatite that we observed in the lowest part of the weathering profile. Table 2 also shows losses of potassium and silicon. The latter could explain the formation of amorphous silica observed in the periphery of residual primary apatites. Manganese and iron exhibit different behaviour types, depending on whether the phlogopite–mica-like gorceixite or the phlogopite–gorceixite matrix is involved. This may be related to the presence of manganese-rich goethite within the gorceixite matrix.

6.4. Magnetite weathering trend

X-ray diffraction patterns show that, during the carbonatite weathering, magnetite is replaced by a mixture of goethite and hematite (Fig. 1F) (type 2 Fe–Mn products), with significant amounts of Mn, Ba and Ti (Table 1A). Isovolume mass balance calculations show that no element, even titanium, can be considered as an isoelement (Table 2). Thus, no mass balance isoelement procedure can be used to quantify bulk chemical transfers during weathering for the magnetite weathering trend.

7. Discussion and conclusions

Rough estimates of local chemical mass balance calculations, made assuming that mineralogical trends exhibit either isovolume or isoelement at the crystal scale, show that high gains and losses of elements prevail in the weathering profile. Elements show different types of behaviour according to the mineralogical trend (i.e., the prevailing primary/secondary minerals) and to the local features of the pore environment. For example, some of the excess magnesium ions may remain in the weathering solutions as highly stable Mg-complexes and can be leached outwards from the weathering profile.

Mass balance calculations also confirm ion micro-transfers from the upper part of the profile (e.g., silicon gain in type 1 Fe–Mn product septae). Chemical transfers during septa formation have been described in several other profiles [20] (see also Merino et al. [23]).

7.1. Movements of REE in the weathering profile

The carbonatite is rich in phosphates and carbonates, with rare aluminium silicates, and is devoid of zircons and REE minerals. This characteristic mineralogy explains why no clay minerals were found within the weathering profile. This is the main feature of this profile, since weathering profiles from the literature are all developed on aluminium silicate-rich rocks. The latter profiles generally exhibit a high content of clays and clay minerals which act as REE traps [24]. Magnetite is highly weathered and our study shows that Ti moves during the weathering processes. This precludes the use of isoelement mass balance calculations on bulk rock samples and implies that we do not know whether the REE behaviour we observed at the crystal scale can be observed at the scale of the outcrop. Movement of the REE during the weathering of the Juquí carbonatite has been observed at the crystal scale. REE mobilization may appear to be different at the outcrop scale, and accumulation/leaching zones may exist within the weathering profile, i.e. where Fe–Mn products are abundant. These poorly crystallized products occur in a pore system and act as REE traps.

The different REE patterns presented by the three samples of mica-like gorceixite may be explained by the presence, in varying amounts, of phases (such as Fe–Mn-rich products) acting as REE traps in the way that clays do [24]. Mass balance calculations
show that several major elements from gorceixite may come from dissolution of primary minerals other than phlogopite (such type 1 and 2 apatites, barite, and magnetite). REE gains exhibited by the gorceixite matrix may also either come from these minerals (especially type 1 and 2 apatites and barite) or be explained as a compensation process relative to the LREE-enriched mica-like gorceixite which is cogenetic with the gorceixite matrix. The LREE and HREE seem to exhibit different behaviour types depending on the way in which gorceixite is formed.

7.2. Relationship between REE content and water/rock ratio

The results presented above indicate that vein- and fissure-filling minerals (calcite, and type 5 and type 6 apatite) are depleted in all REE with respect to the primary minerals from which they derived (Table 1B, Fig. 2). In addition, at least for the type 5 and type 6 apatites and the wavellite, they also show REE distribution curves that are markedly different from those of their respective parent minerals. In contrast, type 3 apatite, which formed within a micropore system by replacing type 1 and type 2 apatites, is only slightly depleted in REE with respect to the primary apatites and is characterized by a REE distribution curve that is essentially identical to that for the primary minerals (with the exception of Er), as is observed for the CO₂ content. The type 1 and type 3 Fe–Mn products are enriched in all REE with respect to the dolomite they replace. Similarly, gorceixite, which formed by pseudomorphic replacement of phlogopite mica or as a recrystallized microcrystalline matrix, is enriched in all REE with respect to its parent mineral.

These observations suggest that a relationship may exist between the content and distribution of REE in secondary minerals and the openness of the porosity system in which they formed (i.e., the water/rock ratio). Our data seem to indicate that precipitation of secondary minerals in open microsystems such as veins and fissures, which are characterized by intense fluid circulations and high water/rock ratios, results in a depletion and fractionation of REE with respect to the associated primary minerals being weathered. In contrast, formation of secondary minerals within intragrain microporosities results in a significant preservation (i.e., chemical memory) of the REE content and distribution of the primary minerals being replaced.

It further appears that pseudomorphic replacements (gorceixite) and poorly crystallized secondary products (Fe–Mn products) are associated with strong REE enrichments. According to this interpretation, the difference in REE enrichment observed between type 1 and type 3 Fe–Mn products may simply be explained by the presence of a greater amount of amorphous components, acting as REE traps, in type 3 Fe–Mn products.

7.3. Ce, Eu and Er anomalies

Ce, Eu and Er anomalies are slight in the secondary minerals (Fig. 2B,C), as they are too in the parent rock and in magmatic minerals (Fig. 2A). Our data suggest neither a mineralogical inheritance nor a selective leaching/concentration of Ce, Eu and Er during the weathering processes. No correlation or anticorrelation between these anomalies is observed. This suggests the occurrence of complex physical and chemical conditions during the weathering.

The anomalies may, therefore, be explained by a type of ‘tetrad effect’ in several of the samples. However, as has been observed by Hidaka et al. and McLennan [25,26] in studies of many other environments, the tetrad effect cannot explain all the REE patterns of the supergene minerals of the Juquía weathering profile. The factors controlling REE patterns during weathering appear to be very complex.

7.4. REE fractionation.

Our petrographical, mineralogical and geochemical analyses show that the REE are fractionated and redistributed within the weathering profile between the different secondary minerals as a result of weathering processes. Our dataset indicates that the La/Yb ratios of the secondary minerals may vary in two ways when compared to the REE content (Table 1B). Phosphates show increasing La/Yb with increasing REE content, while calcite shows decreasing La/Yb ratios with increasing REE content. A similar variation is observed between type 1 Fe–Mn products and type 3 Fe–Mn products, which tends to indicate that
the LREE are preferentially trapped by these products. An opposite variation is observed between the mica-like gorceixite (increasing La/Yb with increasing REE content) and the gorceixite matrix. This may result from different fractionation processes in relation with the different means of formation of these two secondary minerals or from a compensation process between these two cogenetic mineral phases.

Opposing behaviour of the LREE and HREE between fissural phosphates and carbonate secondary minerals may represent differences in the stability constants of REE-carbonate, REE-phosphate and REE-fluoride complexes. Thermodynamic studies show that dissolved fluoride and phosphate complexes rich in HREE are favoured at 25°C under pressures of 1 atm [27–30]. The thermodynamic values are in agreement with the REE distribution curves observed for fissural apatites and wavelite. Calculated stability constants for REE complexes made with carbonate ions also favour the HREE when REE–CO$_3^-$ and REE–(CO$_3$)$_2^-$ complexes are formed. In ‘return’, REE–HCO$_3^-$ complexes appear to favour stability of the MREE complexes in solution. The REE distribution in the secondary low-Mg calcite of Juquiá could be related to such a phenomenon.

7.5. Conclusion

A study of the four mineralogical trends distinguished between primary and secondary minerals in the weathering profile of the Juquía complex provides evidence of local isovolume and isoelement weathering processes. Chemical mass balance calculations show that, except for Al in one mineralogical trend, all the major and trace elements are either leached or concentrated during weathering.

REE behaviour during weathering processes does not solely depend on the parent rock mineralogy and the weathering fluid chemistry. The distribution of REE in secondary minerals may be influenced by the water/rock ratio, as depletion and fractionation of REE prevail in open microsystems when intragrain microporosities result in a significant preservation of the REE content and distribution of the primary mineral being replaced. Pseudomorphic replacement and poorly crystallized minerals are associated with strong REE enrichments associated with high LREE–HREE fractionation.

Moreover, organic matter is abundant in weathering profiles. This may also have an effect on REE complexation and fractionation. For instance, it has been reported that in river waters and in seawater the HREE are preferentially dissolved while the LREE are associated with colloids and/or suspended material [31,32]. However, the direction and magnitude of the effect introduced by the presence of organic matter cannot be assessed at present. This will be an area for our future research.

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